

TITLE OF THE INVENTION

PROCESS AND APPARATUS FOR HIGHWAY MARKING

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CROSS REFERENCE TO RELATED APPLICATIONS

N/A

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR

10

DEVELOPMENT

N/A

BACKGROUND OF THE INVENTION

The methods of "painting" lines on highways or road markings  
15 has changed very little in the past thirty years. Herein the word  
"painting" refers to any method of applying a coating to a road  
surface to form a line or road marking. Prior to this invention,  
there were only three widely used methods to paint lines on  
highways. The most common technique is to spray a chemical paint  
20 on to the road and wait for the paint to dry. The apparatus to  
spray this paint is typically an "air" or "airless" paint machine  
wherein the paint is carried by air and projected to the road  
surface or where the paint is forced through a small hole at very  
high pressure and projected onto the road surface. The "chemical  
25 spray" is the most widely used system to paint lines on highways  
or road markings.

The second technique to paint lines on highways is to apply  
a tape to the road surface wherein this tape is bonded to the road  
surface either with heat or with suitable chemicals. US Patent #  
30 4162862 illustrates a "Pavement Striping Apparatus and Method"  
using a machine to press the tape into hot fresh asphalt. US  
Patent 4236950 illustrates another method of applying a multilayer  
road marking prefabricated tape material.

A third technique is to use a high velocity, oxygen fuel ("HVOF") thermal spray gun to spray a melted power or ceramic powder onto a substrate. This is shown in US Patent 5285967.

Of the three painting methods, the first method of spraying 5 a chemical onto the road surface and waiting for the paint to dry is the predominant technique used today.

The history of line painting indicates that there are at least three properties of "paint" which are important to the highway marking industry: (1) The speed at which the paint dries. 10 (2) The bonding strength of the paint to the road surface. (3) The durability of the paint to withstand the action of automobiles, sand, rain, water etc.

As discussed in US Patent 3,706,684 (Dec. 19, 1972) the first conventional traffic paints were based on drying oil alkyds 15 to which a solvent, such as naphtha or white spirits was added. The paint dries as the solvent is released by evaporation. However, the paint "drying" (oxidation) process "continues and the film becomes progressively harder, resulting in embrittlement and reduction of abrasive resistance thereof causing the film to crack 20 and peel off." The above patent describes "rapid-dry, one-package, epoxy traffic paint compositions which require no curing agent."

As described in US patent 4,765,773:

"The road and highways of the country must be painted 25 frequently with markings indicating dividing lines, turn lanes, cross walks and other safety signs. While these markings are usually applied in the form of fast drying paint, the paint does not dry instantly. Thus a portion of the road or highway must be blocked off for a time sufficient to allow the paint to dry. 30 This, however, can lead to traffic congestion. If the road is not blocked for sufficient time to allow the paint to dry, vehicle traffic can smear the paint making it unsightly. Also in some

instances the traffic will mar the marking to such an extent that the safety message is unclear, which could lead to accidents."

Low-boiling volatile organic solvents evaporate rapidly after application of the paint on the road to provide the desired 5 fast drying characteristics of a freshly applied road marking.

The 4,765,773 patent illustrates the use of microwave energy to hasten the paint drying process of such solvents.

While the low-boiling volatile organic solvents promote rapid drying, "this type of paint formulation tends to expose the 10 workers to the vapors of the organic solvents. Because of these shortcomings and increasingly stringent environmental mandates from governments and communities, it is highly desirable to develop more environmentally friendly coatings or paints while retaining fast drying properties and/or characteristics" (US 15 Patent 6,475,556).

To solve this problem paints have been developed using waterborne rather than solvent based polymers or resins. US patent 6,337,106 describes a method of producing a fast-setting waterborne paint. However, the drying times of waterborne paints 20 are generally longer than those exhibited by the organic solvent based coatings. In addition the waterborne paints are severely limited by the weather and atmospheric conditions at the time of application. Typically the paint cannot be applied when the road surface is wet or when the temperature is below -10 degrees 25 centigrade. Also, the drying time strongly depends upon the relative humidity of the atmosphere in which the paint is applied. A waterborne paint may take several hours or more to dry in high 30 humidity. Lastly the waterborne paints, which are generally known as "rubber based paints", are made from aqueous dispersion polymers. These polymers are generally very "soft" and abrade easily from the road surface due to vehicular traffic, sand and weather erosion.

The above patents all attempt to solve the paint drying problem when using "waterborne" paints and speeding the drying process. The present invention solves the drying problem by not using any solvents in the "painting process".

5 The present invention relates closely to the work done to repair coke ovens, glass furnaces, soaking pots, reheat furnaces and the like which are lined with refractory brick or castings. This process is known today as "ceramic welding".

US Patent 3,800,983 describes a process for forming a  
10 refractory mass by projecting at least one oxidizable substance which burns by combining with oxygen with accompanying evolution of heat and another non-combustible substance which is melted or partially melted by the heat of combustion and projected against the refractory brick . The invention is designed to repair, in  
15 situ, the lining of a furnace while the furnace is operating. Typically the temperature of the walls of the furnace is over 1500 degrees centigrade and the projected powder(s) ignites spontaneously when projected against the hot surface. In this process it is extremely important that both the oxidizable and  
20 non-combustible particles are matched chemically and thermally with the lining of the furnace.

If the thermal properties are not correct, the new refractory mass will crack off from the lining of the furnace due to the differential expansion of the materials. If the chemical  
25 composition is not correct, the new refractory mass will "poison" the melt in the furnace.

In the 3,800,983 patent the oxidizable and non-oxidizable particles are combined as one powdered mixture. The powder is then aspirated from the powder hopper by using pure oxygen under  
30 pressure. The resulting powder-oxygen mixture is then driven through a flexible supply line to a water-cooled lance. The lance is used to project the powder-oxygen mixture against the refractory lining of the furnace to be repaired. The powder-

oxygen mixture ignites spontaneously when it impinges on the hot surface of the oven.

The object of the '983 invention and those that followed is to select the composition of the powders to match the characteristics of the refractory lining and to prevent "flashback" up the lance and back towards the operator of the equipment. "Flashback" is the process wherein the oxygen-powder stream burns so quickly that the flame travels in the reverse direction from the oxygen-powder and causes damage to the equipment and serious hazards to the equipment operator.

US patent 4,792,468 describes a process similar to that above and specifically illustrates the chemical and physical properties of the oxidizable and refractory particles needed to form a substantially crack-free refractory mass on the refractory lining.

US patent 4,946,806 describes a process based upon the 3,800,893 patent wherein the invention provides for the use of zinc metal powder or magnesium metal powder or a mixture of the two as the heat sources in the formation of the refractory mass.

US Patent 5,013,499 describes a method of flame spraying refractory materials (now called "ceramic welding") for in situ repair of furnace linings wherein pure oxygen is used as the aspirating gas and also the accelerating gas and the highly combustible materials can be chromium, aluminum, zirconium or magnesium without flashback. The apparatus is capable of very high deposition rates of material.

US Patent 5,002,805 improves on the chemical composition of the oxidizable and non-oxidizable powders by adding a "fluxing agent" to the mixture.

US Patent 5,202,090 describes an apparatus similar to that shown in US patent 5,013,499. In the '090 patent there are specific details about the mechanical equipment used to mix the powdered material with oxygen and transport the oxygen-powder

combination to the lance. This apparatus also permits very high deposition rates of the refractory material without flashback.

US Patent 5,401,698 describes an improved "Ceramic Welding Powder Mixture" for use in the apparatus shown in the previous 5 patents listed. This mixture requires that at least two metals are used as fuel powder and the refractory powder contains at least magnesia, alumina or chromic oxide.

US Patent 5,686,028 describes a ceramic welding process where the refractory powder is comprised of at least one silicon 10 compound and also that the non-metallic precursor is selected from either CaO, MgO or FeO.

US Patent 5,866,049 is a further improvement on the composition of the ceramic welding powder described in 5,686,028.

US Patent 6,372,288 is a further improvement on the 15 composition of the ceramic welding powder wherein the powder contains at least one substance which enhances production of a vitreous phase in the refractory mass.

#### BRIEF SUMMARY OF THE INVENTION

The invention provides a method of and apparatus for flame spraying refractory material directly onto a road surface to provide a highly reflective, very durable and instant drying "paint" to said road surface. Since the paint contains no solvents and the flame spraying process operates at very high 25 temperatures, the "paint" can be applied under widely varying conditions of temperature and humidity.

The present invention makes use of a ceramic welding process in which a non-combustible ceramic powder is mixed with a metallic fuel and an oxidizer. The mixture is transported to a combustion 30 chamber, ignited and projected against the surface of the road. Alternately, the constituents can be mixed in the combustion chamber. The fuel is typically aluminum powder and the non-combustible ceramic powder is typically silicon or titanium

dioxide. The oxidizer is typically a chemical powder, but can also be pure oxygen. The heat of combustion melts or partially melts the ceramic powder forming a coherent mass that is projected against the road surface, the temperature of the materials causing  
5 the coherent mass to adhere durably to the surface.

The object of the present invention is to present a method of "painting" lines on roads wherein the "paint" dries instantly, adheres durably to the road, has extreme resistance to abrasion and erosion, wind, sand and rain, and inherently safe from  
10 "flashback". This "paint" can be applied at any temperature and under wet and rainy conditions. The operating temperature of the combustion chamber is typically on the order of 3000 degrees Kelvin.  
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#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

The invention will be more fully described in the following detailed description taken in conjunction with the drawings in which:

Fig. 1 is a diagrammatic representation of apparatus in  
20 accordance with the invention;

Fig. 2 is a diagrammatic representation of an alternative embodiment of the apparatus according to the invention;

Fig. 3 is a diagrammatic representation of a further embodiment of the apparatus according to the invention; and  
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Fig. 4 is a diagrammatic representation of one embodiment of a combustion chamber employed in the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

Fig. 1 illustrates a typical embodiment of apparatus  
30 employed in this invention. Hopper (1) contains the metallic fuel powder (2) typically aluminum powder. Hopper (6) contains the powdered chemical oxidizer (7), typically ammonium, potassium or sodium nitrate. The non-combustible ceramic material, typically

silicon or titanium dioxide, can be combined with the fuel powder, the chemical oxidizer or both. Each hopper feeds the powder by gravity into a venturi (3 and 8) fed by air or oxygen (4 and 9). The gas flowing through the venturi is controlled by valves (13) 5 or (14) and aspirates the powder into the air stream. The air streams from both hoppers travel in separate supply lines (5) and (10) and combine in the combustion chamber (11) where the airstreams are mixed and ignited, typically by an electric arc (12) or gas fed pilot light. The resulting combustion melts at 10 least the surface of the non-combustible materials and the air streams project the melted material onto the road surface. The materials form a coherent ceramic or refractory mass that adheres durable to the surface of the road.

In Fig. 1 each hopper has its own supply line (5 and 10) and 15 each supply line goes directly to the top portion of the combustion chamber (11). The combustion chamber has three areas of interest: The top portion (13) is where the metallic fuel and oxidizer mix; the middle portion (14) where the fuel is ignited and high temperature burning takes place; and the lower portion 20 (15) is the lowest temperature portion of the combustion chamber where secondary combustion effects take place.

In Fig. 1, the oxidizer may be pure oxygen supplied from a source (9) and controlled by variable valve (14). The oxygen goes via supply line (10) directly to the combustion chamber (11). In 25 this case no powdered oxidizer is required and the second hopper (6) is not required. It is important that only air be used to aspirate the powdered fuel (2) from the hopper to the combustion chamber (11). The use of air to aspirate the fuel eliminates the possibility of "flashback" to the powdered fuel.

30 Fig. 2 illustrates another method of injecting pure oxygen into the combustion chamber. In this illustration, the powdered fuel is aspirated into the supply line (5) and driven towards the combustion chamber (11). At a point in the supply line (6) that

is close to the combustion chamber, a supply of oxygen is injected into the supply line at point 16 from a source of oxygen (17). This oxygen accelerates the fuel-air mixture and supplies the oxygen necessary for combustion. The injection of oxygen close to 5 the combustion chamber prevents "flashback" since the fuel is aspirated with air up to point number 16. Air is insufficient to maintain combustion of the powdered fuel. Therefore, the powdered 10 fuel-air mixture cannot burn in the reverse direction towards the hopper (1). By injecting the oxygen into the supply line (6), the oxygen aides in the acceleration of the fuel and ceramic powder mixture towards the road surface and also promotes better mixing 15 of the powdered fuel with the oxygen.

This process is inherently safe from "backflash" because the typical aluminum-powdered fuel is transported by air and is 15 separated from the chemical oxidizer until the chemicals are combined in the combustion chamber (11). It is almost impossible to cause aluminum powder to backflash when transported by plain air. In addition, the oxidizer does not burn (or burns very slowly) in air thus preventing any backflash in the supply line 20 (10) transporting the chemical oxidizer.

Another safety feature is that aluminum powder is very difficult to ignite in air. While there are many cautions regarding the use of aluminum powder, the aluminum powder cannot 25 ignite in air unless the flame temperature (from a match etc) exceeds the melting temperature of aluminum oxide (2313K). This inventor has run experiments with several particle sizes of aluminum powder; i.e. 1 micron up to 100 microns and has been unable to ignite any of the powders using a propane torch.

In addition, the non-combustible ceramic powder may be mixed 30 with the metallic combustible powder or the powdered oxidizer. If the non-combustible powder is mixed with the powdered fuel, it will dilute the concentration of the powdered fuel and minimize the possibility of flashback or accidental ignition of the fuel.

According to the various ceramic welding patent disclosures, the quantity of the powdered fuel will typically be less than 15% by weight of the non-combustible ceramic powder.

Fig. 3 illustrates in greater detail the apparatus used in this invention. The hopper (1) contains either the powdered fuel (2) or the powdered oxidizer (7). The powders are fed by a screw conveyer (18) which is driven by a variable speed motor (19). The screw conveyor feeds into a funnel (20) which is in fluid communication with an aspirator (3) into which a stream of air from source (4) is directed. The rate of flow of the air stream is controlled by valve (13) in series with the air source (4). The venturi aspirates the powdered fuel from the funnel into the supply line (5) wherein the entrained particles are delivered to the combustion chamber (11). The variable speed motor along with the screw conveyor and the air control valve (13) provide an accurate means of dispensing the powdered fuel(s) and oxidizer to the combustion chamber and varying the rate of combustion and deposition of the refractory materials onto the road surface. The variable speed motor and air control value (13) are controlled by a device which measures the speed of the "line painting machine" relative to the surface of the road. In this manner the thickness of the deposition on the road surface can be controlled independently of the speed of the line painting apparatus relative to the surface of the road.

The choice of oxidizing chemical is very important to the safety and economics of this line painting process. The oxidizing chemical must be low cost, readily available, non-toxic, and burn with a flame temperature sufficiently high to soften or melt the ceramic materials used in this process. The following chemicals were considered:

Ammonium Perchlorate (NH<sub>4</sub>ClO<sub>4</sub>)

Ammonium Nitrate (NH<sub>4</sub>NO<sub>3</sub>)

Potassium Nitrate (KNO<sub>3</sub>)

Sodium Nitrate (NaNO<sub>3</sub>)  
Potassium Perchlorate (KCLO<sub>4</sub>)  
Sodium Perchlorate (NaCLO<sub>4</sub>)  
Potassium Chlorate (KCLO<sub>3</sub>)  
5      Sodium Chlorate (NaCLO<sub>3</sub>)  
Air  
Pure oxygen

Ammonium Perchlorate is a well known and well characterized oxidizer used in solid state rocket fuels. It is the oxidizer for 10 the solid rocket boosters for the space shuttle. It is relatively expensive and made by only one company in the United States. The combustion products are primarily NO and a small amount of NO<sub>2</sub>, chlorine and hydrogen chloride (HCL), all of which are toxic. Therefore, Ammonium Perchlorate was ruled out for use as the 15 oxidizer in this application.

Ammonium Nitrate (NH<sub>4</sub>NO<sub>3</sub>) is one of the better oxidizers because it contains no chlorine and therefore produces no HCL. It may generate toxic amounts of NO, although the concentration of the NO when combined with free air is likely to be very low. 20 Ammonium Nitrate is also known as fertilizer and widely used in explosives. It is widely available and inexpensive. However, it takes 4.45 pounds of ammonium nitrate to burn one pound of aluminum and therefore ammonium nitrate will require larger volumes and weight than other potential oxidizers.

Potassium Nitrate (KNO<sub>3</sub>) and Sodium Nitrate (NaNO<sub>3</sub>) are 25 widely available, very inexpensive and will also generate a toxic amount of NO. Again, it is expected that the NO will be very much diluted with free air in the operation of this machine. Both Potassium Nitrate and Sodium Nitrate will generate byproducts 30 which will react with air to create hydroxides. These hydroxides are soluble in water and may (or may not) cause problems with the deposition and adherence of the refractory material on the road surface. Only 2.25 pounds of KNO<sub>3</sub> are required to burn one pound

of aluminum. Therefore, KNO<sub>3</sub> is a very good candidate for the oxidizer.

Sodium Nitrate (NaNO<sub>3</sub>) has very similar properties to KNO<sub>3</sub>. It is readily available, low cost and only requires 1.89 pounds of 5 KNO<sub>3</sub> to burn one pound of aluminum.

The other Perchlorate and Chlorates are similar in performance and combustion properties to Sodium and Potassium Nitrate and will also generate byproducts that are water soluble. They are more expensive and less available than Sodium and 10 Potassium Nitrate.

Air is a very good candidate for use as the oxidizer. Obviously it is readily available and only requires a compressor. The question is can sufficient air be injected into the system to supply sufficient oxygen for the combustion and also not drain too 15 much of the heat away.

Pure oxygen is an excellent candidate for the oxidizer. Using pure oxygen would create a process very similar to ceramic welding. There are no toxic byproducts and the valves and controls are inexpensive. Pure oxygen is very inexpensive and readily 20 available. If compressed oxygen (as a gas) is used, the containers are very large and heavy relative to the amount of oxygen stored. Also, the problem of "flashback" must be addressed.

Liquid oxygen is a very good candidate for large volume 25 highway painting applications. It is very inexpensive and widely available. The only problem is the storage and handling of the LOX.

The following non-combustible ceramic materials were considered for use as the "paint pigment" in this apparatus:  
30 Silicon Dioxide  
Titanium Dioxide  
Aluminum Oxide  
Chromium Oxide produced from refused grain brick.

Magnesium Oxide  
Magnesite regenerate  
Corhart-Zac  
Al<sub>2</sub>O<sub>3</sub>-/Bauxite-Regenerate

- 5       The prime criteria for the selection of the "paint pigment" are cost and availability. Titanium Dioxide is the prime pigment used in white paints, is readily available, and is very low in cost. Aluminum Oxide is also readily available, but is much more costly than titanium dioxide. Silicon dioxide is normally known as
- 10      "sand" and may be the least expensive of all of the "paint pigments". Chromium Oxide, if produced from refused grain brick, is also a low cost ceramic material, but may not be consistent in its mixture. Magnesium Oxide may be used in small amount to enhance the thermal properties of the final paint product.
- 15      Magnesite regenerate, Corhart-Zac and Bauxite-Regenerate are recycled refractory products that were previously used in high temperature furnaces.

In addition to the selection of low cost ceramic materials for use as "paint pigment", there is a requirement for coloring 20 materials to produce the colors of yellow, blue and red on road surfaces. These coloring materials may be pre-mixed with the ceramic powder or powdered fuel, or may be added to the combustion chamber via a separate supply line.

Since the oxidizer powders tend to be hygroscopic, it is 25 necessary to add "anti-caking" agents to the powder to prevent the formation of clumps, which inhibits the powder from flowing smoothly. The "anti-caking" agent is also known as a "flow" agent. The typical flow agent is TCP (Tri-calcium Phosphate), although others are well known in the art.

30      Fig. 4 illustrates one aspect of the combustion chamber (11). Since the apparatus operates at extremely highly temperature, typically above 3000 degrees Kelvin, it is important that the combustion chamber be designed to be low cost and have a

very long life at elevated temperature. Fig. 4 illustrates the use of small venturies (21) built into the sides of the combustion chamber. As the combustion products are projected from the combustion chamber (11), the velocity of the combustion gases  
5 create a partial vacuum on the inside surface of the combustion chamber. Cooler air is sucked into the venturi entrance (21) and flows along the inside of the combustion chamber (22). This air both cools the inside surface of the combustion chamber and also reduces the build up of residual products on the inside of the  
10 combustion chamber.

The invention is not to be limited by what has been particularly shown and described and is to encompass the full spirit and scope of the appended claims.

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